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TEMPERATURE-DEPENDENT DEPHASING OF DELOCALIZED DIMER STATES OF PENTACENE IN *p*-TERPHENYL: PICOSECOND PHOTON ECHO EXPERIMENTS

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Optical dephasing of pentacene dimers in *p*-terphenyl is studied. Dimer states R_3 and R_4 exhibit an exponential temperature activation of T_2' which is inconsistent with a mechanism involving scattering between delocalized dimer states. Other dephasing mechanisms are discussed. An upper limit is placed on the relaxation rate from the upper dimer state, R_1 , to R_3 .

1. Introduction

There has been an increasing amount of experimental and theoretical interest in dimer coherence in mixed crystals [1,2]. These dimers consist of isolated pairs of guest molecules substitutionally imbedded in a host crystalline lattice. The relative orientations of the molecules in the dimer pair are usually taken to be similar to the orientation of host molecules in the pure crystal. Thus, there are a variety of possible dimer pairs having various intermolecular interactions. An excited dimer has been referred to as a "mini-exciton". The dimer provides the simplest system to study the nature of delocalized electronic states and their dynamic interactions with the environment.

The first direct measurement of dimer coherence via photon echo experiments has recently been reported [2] for the system of pentacene dimers in a *p*-terphenyl host crystal. Only the coherence times for the dimer states shifted by intermolecular interactions to the red of the pentacene monomers (red dimer states) were measured. The states shifted to the blue of the monomer $S_0 \rightarrow S_1$ transition (blue dimer states) are masked by the intense phonon sideband of the monomer. Here we report the observation of several blue dimer states which were detect-

ed using a type of photon echo excitation spectroscopy. Detection of these blue dimer states permits examination of a wider variety of pentacene dimers. The differences between the dimer crystal shifts and the monomer crystal shift are also discussed.

In addition, an extensive temperature dependence of T_2' (the dephasing time excluding the excited state to ground state lifetime contribution) of the red dimer state, R_3 [2], is reported for the temperature range 1.3–16 K. Photon echo decay measurements provided T_2' at low temperatures in which the homogeneous line is masked by inhomogeneous broadening. At higher temperatures, T_2' was determined from line-shape studies of the transmission spectra. Results from preliminary photon echo measurements on another red dimer state, R_4 , are also presented. The potentially important temperature-dependent dephasing mechanisms, phonon-induced scattering between the delocalized dimer states and other phonon-induced scattering (T_1) and pure dephasing (T_2^*) processes, were analyzed using optical Redfield theory. The evidence demonstrates that scattering between delocalized dimer states is not responsible for the temperature-dependent dephasing in this system.

2. Experimental

The picosecond photon echo system used in these experiments has been described in detail else-

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where [3]. The requisite picosecond light pulses were provided by a mode-locked, cavity-dumped dye laser synchronously pumped by the frequency-doubled output of a cw-pumped acousto-optically mode-locked and *Q*-switched Nd : YAG laser. This dye laser system provides a stable source of 30 ps, 20 μ J pulses at a 400 Hz repetition rate.

A dye laser single pulse is split into two excitation pulses of appropriate energies and variable temporal delays for the photon echo experiment. In these experiments, collinear excitation beams were used. The generated echo signal is temporally, spatially, and frequency selected by frequency summing with a single 80 ps IR pulse from the YAG laser. The up-converted echo signal is then detected with a phototube.

The sample was mounted on a heating block located in a liquid-helium dewar. Cold helium gas was allowed to flow over the sample. The temperature was controlled by varying the flow of helium gas and the power delivered to the heating block. The temperature was measured with a Au + 0.07% Fe versus chromel thermocouple in thermal contact with the sample.

Polarized transmission spectra were obtained using a high-pressure xenon arc lamp, a 1 m Spex scanning monochromator, and a 1P28 phototube.

The pentacene in *p*-terphenyl mixed crystals were grown by the Bridgman technique using extensively zone-refined *p*-terphenyl. The pentacene, obtained from Aldrich, was vacuum sublimed once before use.

3. Results and discussion

Fig. 1 shows a transmission spectrum of a high concentration crystal of pentacene in *p*-terphenyl in the vicinity of the $S_0 \rightarrow S_1$ absorption origins, O_1 and O_2 , of pentacene monomers [13]. The O_1 and O_2 origins coalesce into a broad and flat-topped peak because of the very high monomer concentration resulting in zero transmittance. To the red of the broad origins lie three well-resolved peaks, labeled R_3 , R_4 , and R_5 , which have previously been shown to arise from pentacene dimer states [2]. Several other less resolved peaks, labeled R_1 and R_2 , can also be observed on the side of the monomer absorption [2].

The dimer absorptions are shifted from the monomer origin for two reasons [2]. First, the dipole-di-

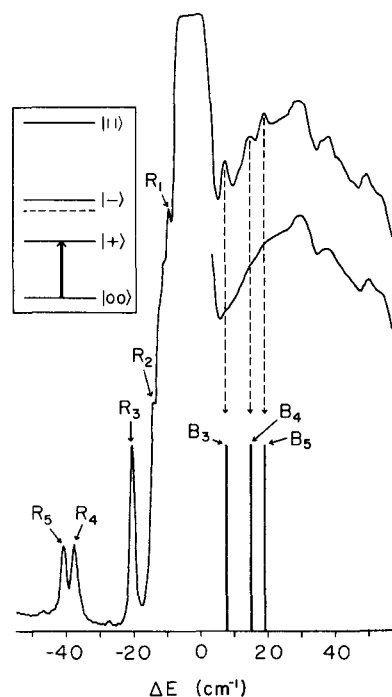


Fig. 1. Transmission spectrum in the region about the pentacene in *p*-terphenyl $S_0 \rightarrow S_1$ monomer origin at 1.4 K. The high concentration results in a broad flat origin. The zero of energy is taken between the monomer O_1 and O_2 site origins. To the red, five pentacene dimer peaks are labeled R_1 through R_5 . To the blue, three dimer states, B_3 through B_5 , located by photon echo excitation spectroscopy, are indicated. Two phonon sideband spectra are shown. In the upper very high concentration spectrum, the blue dimer states appear as small features. For a sample of lower concentration shown in the lower spectrum, these blue dimer features are absent but still echo detectable. The inset illustrates a dimer level scheme with $|\Delta D| < |\beta|$. See text.

pole interaction between the pair of pentacene monomers (β) will split the states by an amount which depends on β , shifting one to the blue and one to the red. If the two monomer states are degenerate or near degenerate, the splitting is 2β . Second, the crystal shift (due to van der Waals interactions with the environment) will generally be different for a dimer and a monomer. This difference in crystal shift (ΔD) will displace the center of gravity of a pair of dimer states from the monomer origin. If $|\Delta D| < |\beta|$, the dimer will have one state to the red and one state to the blue of the monomer origin. However, if $|\Delta D| > |\beta|$ both dimer states will be either to the red or to the blue of the monomer line, depending on the sign of

ΔD . The case where $|\Delta D| < |\beta|$ is illustrated schematically in the inset of fig. 1.

As can be seen from fig. 1, the intense monomer phonon sideband obscures observation of blue dimer states by conventional transmission spectroscopy. (Note: "blue dimer state" refers to any dimer state shifted to the blue of the origin.) We were able to locate several blue dimer states buried under the phonon sideband using photon echo excitation spectroscopy. The phonon sideband did not give an echo signal within the time resolution of the instrument (50 ps). However, at 1.4 K, it was anticipated and subsequently confirmed that some blue dimer states would have nanosecond coherence decay times similar to the observed red dimer states. Thus, several blue dimer states were located by directing a photon echo pulse sequence with a fixed pulse separation of ≈ 1 ns into the sample and recording the intensity of the photon echo signal as a function of excitation frequency. Three well-defined peaks were observed. These are indicated by the solid lines in fig. 1 labeled B_3 , B_4 , and B_5 . Like the red dimer states [2], these peaks did not have a linear concentration dependence. Thus, by using T_2 -selective spectroscopy, it was possible to locate states which were otherwise masked by the intense phonon sideband.

The observation of blue dimer states is consistent with the possibility that dimer states could be shifted to the blue as well as to the red of the monomer absorption. To date, a detailed assignment of the observed peaks into associated pairs of dimer states has not been made with the exception of R_1 and R_3 . Recent coherent Stokes Raman scattering (CSRS) experiments demonstrated conclusively that R_1 and R_3 form a dimer pair [4]. This gives a R_1/R_3 dimer splitting of 12.0 cm^{-1} and a shift of 14 cm^{-1} relative to the zero of energy defined in fig. 1. Experiments to assign the other peaks are in progress [4].

To determine the nature of the dynamic interactions of the delocalized dimer states with the environment, a temperature-dependent study of the dimer dephasing time was conducted. At the lowest temperatures (1.4–2.2 K) T_2 , as determined by photon echo experiments for R_3 , R_4 , and R_5 , is temperature independent. Table 1 lists 2τ (twice the fluorescence lifetime), T_2 , and T'_2 . (The T_2 and T'_2 numbers are slightly different than those originally reported [2]. The original measurements were marred by the recently

Table 1

The wavelength, twice the fluorescence decay time 2τ , photon echo decay time T_2 , and non-lifetime dephasing time T'_2 ($1/T'_2 = 1/T_2 - 1/2\tau$) of dimer states R_1 – R_5 and B_3 – B_5

Dimer state	λ (Å)	2τ (ns)	T_2 (ns)	T'_2 (ns)
R_5	5935.1	31	14	26
R_4	5934.0	33	22	66
R_3	5928.0	39	32	178
R_2	5925.7	—	—	—
R_1	5923.8	—	—	—
B_3	5918.0	—	—	—
B_4	5915.4	—	—	—
B_5	5914.0	—	—	—

discovered effect of the sample's optical density on the photon echo decay time [5].) Table 1 shows that T_2 is close to the 2τ lifetime limit. Thus, the dimers are long-lived coherent delocalized states. The reason for the temperature-independent difference between T_2 and 2τ , which has also been observed in monomer systems [6], is not understood, although one possibility has been put forward [7] and additional experiments are currently in progress.

Fig. 2 shows a detailed temperature dependence of T'_2 for the R_3 dimer state. Photon echo decay were recorded at various temperatures between 1.4 and 7 K which provided direct measurements of T_2 and thus T'_2 over two orders of magnitude. At higher temperatures, the homogeneous linewidth became significant compared to the inhomogeneous linewidth, and T'_2 was obtained from optical lineshape measurements in the following manner. The optical lineshape was recorded at a temperature at which it was clear from photon echo measurements that there was no contribution from the homogeneous linewidth. This lineshape is the convolution of the inhomogeneous lineshape and the monochromator slit function. A lineshape recorded at a higher temperature was then fit by convolving the low-temperature lineshape with a lorentzian. The width of the lorentzian which gave the best fit provided T'_2 .

Fig. 2 shows that a log plot of T'_2 versus $1/T$ for R_3 gives a straight line over many orders of magnitude of T'_2 . This indicates an exponentially activated process with an activation energy, $\Delta E = 21 \pm 1 \text{ cm}^{-1}$. A preliminary study of the R_4 line using photon echo decay measurements yields a similar activation energy of $\approx 20 \text{ cm}^{-1}$.

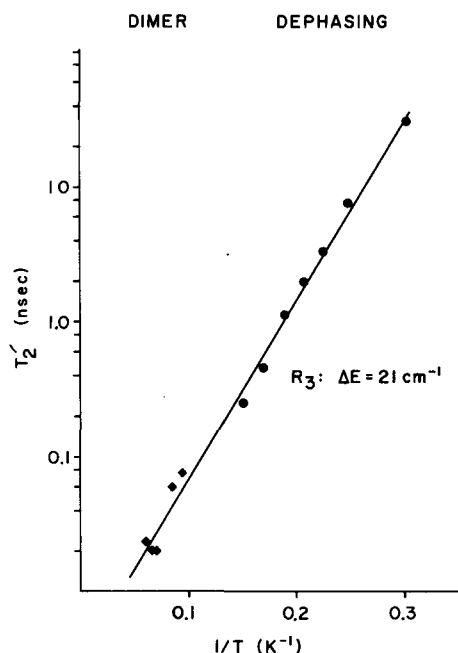


Fig. 2. Temperature dependence of T_2' (the dephasing time excluding the excited state to ground state lifetime contribution) of pentacene dimer state R_3 in *p*-terphenyl. Results from 3.3 to 7 K were obtained from photon echo decay measurements (circles). Lineshape analysis of the transmission spectra provided T_2' from 10.6 to 16 K (squares). The solid line is the best fit to the data, giving an exponential activation energy of $\Delta E = 21 \pm 1 \text{ cm}^{-1}$ and a pre-exponential factor of 3.1 ps.

The observation of an exponential temperature activation of T_2' with phonon-like activation energies is consistent with the following dephasing mechanisms (see fig. 3):

(A) *Scattering between delocalized dimer states.* In a detailed calculation using optical Redfield theory, Lee and Fayer [8] have demonstrated that single-phonon scattering processes between the two dimer states (analogous to exciton $k \rightarrow k$, scattering in pure crystals) induced by linear electron-phonon coupling will produce an exponential temperature behavior with an activation energy given by the dimer splitting. Using a less detailed but more general calculation, Skinner et al. [9] have shown that, regardless of the type of electron-phonon coupling, scattering between the two dimer states arising from single-phonon processes will produce an exponential activation with the dimer splitting.

(B) *Scattering to librational states.* An effective

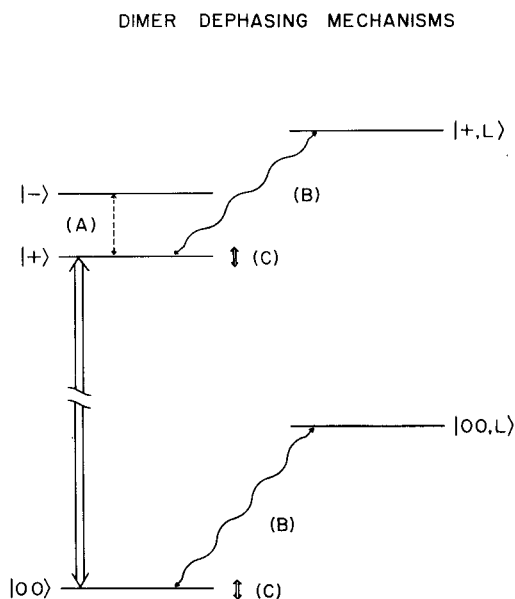


Fig. 3. Dimer dephasing mechanisms. $|00\rangle$, $|+\rangle$, and $|-\rangle$ are the ground and delocalized dimer states, respectively. $|00,L\rangle$ and $|+,L\rangle$ are the mini-librons associated with $|00\rangle$ and $|+\rangle$. Mechanism (A) involves phonon-induced scattering between the two dimer states (a T_1 process). Mechanism (B) involves phonon-induced scattering of the dimer ground and excited states to mini-librons (a T_1 process). (Note that only one of each pair of mini-libron states is shown in the figure.) Mechanism (C) involves quadratic coupling to an optical phonon band (a T_2^* process).

four-level system can be defined (in analogy with that used for monomers by de Bree and Wiersma [10]) consisting of the dimer ground and lowest excited states and a degenerate pair of librational states (mini-librons) associated with each of these electronic states. (The complete six-level system with non-degenerate mini-librons is discussed elsewhere [8].) Scattering to mini-librons results in a bi-exponential temperature behavior with activation energies given by the librational energies in the dimer ground and excited states [8]. However this will appear as a single exponential if the mini-libron energies in the ground and excited states are comparable (but sufficiently different to preclude coherence transfer) [11].

(C) *Phonon-induced pure dephasing.* Linear electron-phonon coupling to harmonic phonons does not contribute to monomer pure dephasing. This is also true for dimers. However, quadratic electron-phonon coupling can result in pure dephasing. Quadra-

tic coupling to acoustic phonons at low temperatures $\omega_D \gg kT/\hbar$ results in the familiar T^7 temperature dependence of T_2^* for the dimer. Since this is clearly not observed, this leaves quadratic coupling to optical phonons. It can be shown that various choices for the density of optical phonon states result in a temperature dependence of T_2^* that is well approximated by an exponential [8].

With the experimental information available, some conclusions can be drawn about the dynamics of this system. First, the experimental determination that R_3 is paired with R_1 gives a dimer splitting of 12.0 cm^{-1} . Within the context of mechanism (A), this splitting is inconsistent with the observed activation energy of $21 \pm 1 \text{ cm}^{-1}$. Second, it has been established that monomer librations are responsible for the temperature-dependent dephasing of pentacene monomers in naphthalene host crystals [11]. The energy of this monomer librational mode was shown to be 18 cm^{-1} in the ground state (S_0) and 14 cm^{-1} in the excited state (S_1). The magnitudes of the observed pentacene in *p*-terphenyl dimer activation energies (21 and 20 cm^{-1} for R_3 and R_4 , respectively) are similar to the pentacene monomer librational energies in naphthalene. Third, recent Raman spectra of *p*-terphenyl pure crystals at 29 K reveal the existence of several low-energy optical phonons, specifically one at 20.5 cm^{-1} [14]. By an appropriate choice of optical phonon state density and bandwidth (encompassing the 20.5 cm^{-1} optical phonon) a quasi-exponential temperature behavior results with an apparent activation energy consistent with the observed $21 \pm 1 \text{ cm}^{-1}$ activation of the R_3 dimer state.

The above considerations eliminate scattering between delocalized dimer states as the dominant dephasing mechanism. The possible mechanisms are scattering to mini-librons (a T_1 process) or quadratic coupling to an optical phonon band (a T_2^* process). The existence of a 20.5 cm^{-1} optical phonon makes it tempting to assume that the T_2^* process dominates. However, pentacene monomers in *p*-terphenyl dephase with a 30 cm^{-1} activation energy which has been ascribed to scattering to a monomer libration [11]. The question of the correct mechanism remains open, but the following points are relevant. Phonon-induced pure dephasing of the dimer arises from modulation of the dipole-dipole interaction as well as the site crystal shift, whereas pure dephasing of the

monomer arises only from modulation of the site crystal shift, i.e. a pure dephasing mechanism (modulation of the dipole-dipole interaction) exists for the dimer which does not exist for the monomer. Also, the possibility exists that pentacene dimers and monomers in *p*-terphenyl both dephase via coupling to optical phonons. A reported 38.5 cm^{-1} optical phonon [14], given the correct band structure, can account for the observed monomer temperature dependence [8]. Experiments in progress will help pin down the dephasing mechanism.

It is interesting to note that the dimer splitting (12.0 cm^{-1}) is significantly smaller than the activation energy (21 cm^{-1}), yet scattering between delocalized dimer states is not the dominant dephasing mechanism. It is expected that some scattering between delocalized dimer states does occur. If this mechanism were operative to any significant extent the experimental data would not be a single exponential throughout the temperature range studied. Comparing the experimental data to the calculations of the temperature dependence with two mechanisms operative, and using a detailed balance argument allow us to place a lower limit of 0.1 ns on the lifetime (due to phonon-induced scattering between the dimer states) of the upper dimer state R_1 .

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